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[Title of the document] Specification

[Title of the invention] Resin moldings for gas and/or liquid barrier parts

[Claims]

[Claim 1]

A resin molding for gas and/or liquid barrier parts comprising a resin composition that consists of 100 parts by weight of a resin composition component consisting of (a) 5-80 vol% of polyolefin resin and (b) 95-20 vol% of polyphenylene sulfide resin, in combination with (c) 0-200 parts by weight of an inorganic filler, wherein the phase structure as observed by electron microscopy comprises (b) a matrix phase (continuous phase) of said polyphenylene sulfide resin and (a) a distribution phase of said polyolefin resin.

[Claim 2]

A resin molding for gas and/or liquid barrier parts according to claim 1 wherein said (a) polyolefin resin and (b) polyphenylene sulfide resin account for 55-80 vol% and 45-20 vol%, respectively.

[Claim 3]

A resin molding for gas and/or liquid barrier parts according to claim 1 wherein said (a) polyolefin resin and (b) polyphenylene sulfide resin account for 60-75 vol% and 40-25 vol%, respectively.

[Claim 4]

A resin molding for gas and/or liquid barrier parts comprising a resin composition that consists of 100 parts by weight of a resin composition component consisting of (a) 15-85 vol% of polyolefin resin and (b) 85-15 vol% of polyphenylene sulfide resin, in combination with (c) 0-200 parts by weight of an inorganic filler, wherein the phase structure as observed by electron microscopy comprises (b) a phase of said polyphenylene sulfide resin and (a) a phase of said polyolefin resin, both in the form of a virtually

continuous phase.

[Claim 5]

A resin molding for gas and/or liquid barrier parts comprising a resin composition that consists of 100 parts by weight of a resin composition component consisting of (a) 55-95 vol% of polyolefin resin and (b) 45-5 vol% of polyphenylene sulfide resin, in combination with (c) 0-200 parts by weight of an inorganic filler, wherein the phase structure as observed by electron microscopy comprises (a) a continuous phase of said polyolefin resin and (b) a zonal distribution phase of said polyphenylene sulfide resin.

[Claim 6]

A resin molding for gas and/or liquid barrier parts according to any of claims 1-5 wherein said (a) polyolefin resin is at least one selected from the group consisting of polyethylene; polypropylene; ethylene/α-olefin copolymers; copolymers of ethylene and/or propylene, and an unsaturated carboxylic acid and/or an unsaturated carboxylate; and copolymers of ethylene and/or propylene, and an unsaturated carboxylic acid and/or an unsaturated carboxylate, with at least part of the carboxyl groups being modified into metal salts.

[Claim 7]

A resin molding for gas and/or liquid barrier parts according to any of claims 1-6 wherein the amount of said inorganic filler used as component (c) is in the range of 5-200 parts by weight.

[Claim 8]

A container, and attachment thereof, for transportation and/or storage of liquid chemicals and/or gas, comprising a resin molding for gas and/or liquid barrier parts as described in any of claims 1-7.

[Claim 9]

A resin molding for gas and/or liquid barrier parts according to any of claims 1-8 produced by a molding method selected from the group consisting of injection molding, injection compression molding, and compression molding.

[Detailed description of the invention]

[0001]

[Technical field of the invention]

The present invention relates to moldings that have good barrier properties against gas and/or liquid. In particular, the invention relates to resin moldings that comprise a specific phase structure consisting of polyolefin resin and polyphenylene sulfide resin (hereafter abbreviated as PPS resin) to develop specifically enhanced barrier properties and high moldability, and accordingly serve as good material for gas and/or liquid barrier parts.

[0002]

[Prior art]

Polyolefin resins such as polyethylene and polypropylenes have been widely used as the most common plastic material for sundry goods, toys, machine parts, electric and electronic parts, and automobile parts. There have been increasingly various resin moldings in recent years that require gas barrier (permeation resistant) properties for prevention of leakage of contents and entry of external air to ensure safety, storage stability, and environmental pollution prevention, but conventional polyolefin resin products do not have sufficient barrier properties against liquid chemicals and gas, imposing limitations on the scope of their applications and leading to demands for improved materials.

[0003]

To supplement such physical properties of polyolefin resin, resin compositions and moldings that consist of polyolefin resin and

polyamide resin, which has good barrier properties, have been proposed recently. However, though polyamide certainly works to increase the barrier properties as compared to polyolefin resin used alone, further technical improvement is currently called for to produce material with further enhanced barrier properties.

[0004]

[Problems to be solved by the invention]

The goal of the present invention is to provide polyolefin-based material with enhanced barrier properties, and furthermore provide resin moldings that have specifically-enhanced barrier properties against liquid chemicals and gas, while maintaining intrinsic features of polyolefin resin such as high toughness and moldability, particularly focusing on production of polyolefin-PPS resin moldings suitable as material for gas and/or liquid barrier parts.

[0005]

[Means of solving the problems]

Thus, the present inventors have carried out studies aiming to solve the above problems and achieved the present invention after finding that the goal described above can be met by a resin molding produced by combining polyolefin resin and PPS resin at a specific ratio, followed by addition of an inorganic filler as required, wherein the distribution of resins in the phase structure is controlled so that the PPS resin forms a continuous phase in the molding.

[0006]

Specifically, the present invention provides: (1) a resin molding for gas and/or liquid barrier parts comprising a resin composition that consists of 100 parts by weight of a resin composition component consisting of (a) 5-80 vol% of polyolefin resin and (b) 95-20 vol% of polyphenylene sulfide resin, in combination with (c) 0-200 parts by weight of an inorganic filler, wherein the phase structure as

observed by electron microscopy comprises (b) a matrix phase (continuous phase) of said polyphenylene sulfide resin and (a) a distribution phase of said polyolefin resin;

(2) a resin molding for gas and/or liquid barrier parts according to item (1) above, wherein said (a) polyolefin resin and said (b) polyphenylene sulfide resin account for 55-80 vol% and 45-20 vol%, respectively;

(3) a resin molding for gas and/or liquid barrier parts according to item (1) above, wherein said (a) polyolefin resin and said (b) polyphenylene sulfide resin account for 60-75 vol% and 40-25 vol%, respectively;

(4) a resin molding for gas and/or liquid barrier parts comprising a resin composition that consists of 100 parts by weight of a resin composition component consisting of (a) 15-85 vol% of polyolefin resin and (b) 85-15 vol% of polyphenylene sulfide resin, in combination with (c) 0-200 parts by weight of an inorganic filler, wherein the phase structure as observed by electron microscopy comprises (b) a phase of said polyphenylene sulfide resin and (a) a phase of said polyolefin resin, both in the form of a virtually continuous phase;

(5) a resin molding for gas and/or liquid barrier parts comprising a resin composition that consists of 100 parts by weight of a resin composition component consisting of (a) 55-95 vol% of polyolefin resin and (b) 45-5 vol% of polyphenylene sulfide resin, in combination with (c) 0-200 parts by weight of an inorganic filler, wherein the phase structure as observed by electron microscopy comprises (a) a continuous phase of said polyolefin resin and (b) a zonal distribution phase of said polyphenylene sulfide resin;

(6) a resin molding for gas and/or liquid barrier parts according to any of items from (1) to (5) above, wherein said (a) polyolefin

resin is at least one selected from the group consisting of polyethylene; polypropylene; ethylene/ α -olefin copolymers; copolymers of ethylene and/or propylene, and an unsaturated carboxylic acid and/or an unsaturated carboxylate; and copolymers of ethylene and/or propylene, and an unsaturated carboxylic acid and/or an unsaturated carboxylate, with at least part of the carboxyl groups being modified into metal salts;

(7) a resin molding for gas and/or liquid barrier parts according to any of items from (1) to (6) above, wherein the amount of said inorganic filler added as component (c) is in the range of 5-200 parts by weight;

(8) a container, and attachment thereof, for transportation and/or storage of liquid chemicals and/or gas produced by processing a resin molding for gas and/or liquid barrier parts as described in any of from (1) to (7) above; and

(9) a resin molding for gas and/or liquid barrier parts according to any of items from (1) to (8) above, which is produced by a molding method selected from the group consisting of injection molding, injection compression molding, and compression molding.

[0007]

[Modes for carrying out the invention]

Good modes for carrying out the invention are described below. For the invention, weight refers to mass.

[0008]

Useful polyolefin type resins to be used as component (a) for the present invention include homopolymers including polyethylene, polypropylene, polystyrene, polyacrylate, polymethacrylate, poly-1-butene, poly-1-pentene and polymethylpentene; ethylene/ α -olefin copolymer; homopolymers of vinyl alcohol esters; polymers produced by hydrolyzing at least part of a homopolymer

of a vinyl alcohol ester; polymers produced by hydrolyzing at least part of a copolymer of ethylene and/or propylene, and a vinyl alcohol ester; copolymers of ethylene and/or propylene, and an unsaturated carboxylic acid and/or an unsaturated carboxylate; copolymers of ethylene and/or propylene, and an unsaturated carboxylic acid and/or an unsaturated carboxylate, with at least part of the carboxyl groups being modified into metal salts; block copolymers of a conjugated diene and an aromatic vinyl hydrocarbon; and hydrides of said block copolymers.

[0009]

Preferred ones include polyethylene, polypropylene, ethylene/ α -olefin copolymer, ethylene/(meth)acrylic acid copolymer, and ethylene/(meth)acrylic acid copolymer with at least part of the carboxyl groups being in the form of a metal salt; of which low, medium and high density polyethylene, polypropylene, and ethylene/ α -olefin copolymer are particularly preferred.

[0010]

There are no specific limitations on the structure of polypropylene, and isotactic, atactic, and syndiotactic ones can be used appropriately. In addition to homopolymers, block and random copolymers consisting of 70 wt% or more propylene and other olefin components.

[0011]

Said ethylene/ α -olefin copolymer refers to one or more copolymers of ethylene and α -olefins with 3-20 carbon atoms, and said α -olefins with 3-20 carbon atoms include propylene, 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene, 1-nonene, 1-decene, 1-undecene, 1-dodecen, 1-tridecene, 1-tetradecene, 1-pentadecene, 1-hexadecene, 1-heptadecene, 1-octadecene, 1-nonadecen, 1-eicosen, 3-methyl-1-butene, 3-methyl-1-pentene, 3-ethyl-1-pentene,

4-methyl-1-pentene, 4-methyl-1-hexene, 4,4-dimethyl-1-hexene, 4,4-dimethyl-1-pentene, 4-ethyl-1-hexene, 3-ethyl-1-hexene, 9-methyl-1-decene, 11-methyl-1-dodecen, 12-ethyl-1-tetradecene, and combinations thereof. Of these α -olefins, copolymers comprising an α -olefin with 3-12 carbon atoms are preferred in terms of mechanical strength. In said ethylene/ α -olefin copolymers, α -olefins should preferably account for 1-30 mol%, more preferably 2-25 mol%, and still more preferably 3-20 mol%.

[0012]

Further, they may be copolymers with one or more nonconjugated diene such as 1,4-hexadiene, dicyclopentadiene, 2,5-norbornadiene, 5-ethylidene norbornene, 5-ethyl-2,5-norbornadiene, and 5-(1'-propenyl)-2-norbornene.

[0013]

The unsaturated carboxylic acid used in said copolymers of propylene and/or ethylene and an unsaturated carboxylic acid and/or an unsaturated carboxylic ester is either an acrylic acid or a methacrylate, or a mixture thereof, while the unsaturated carboxylic ester is a methyl ester, ethyl ester, propyl ester, butyl ester, pentyl ester, hexyl ester, heptyl ester, octyl ester, nonyl ester, or decyl ester of an unsaturated carboxylic acid as described above, or a mixture thereof, preferred copolymers being those produced from ethylene and a methacrylic acid and those produced from ethylene, a methacrylic acid and an acrylic ester.

[0014]

Moreover, for purposes of the present invention, said (a) polyolefin resin may be a polyolefin resin as described above modified with one or more derivative of an unsaturated carboxylic acid. The use of a modified polyolefin resin as described above leads to an increased compatibility of the polyolefin resin used and enhanced

controllability of the phase structure of the resulting resin composition, which serve to achieve good barrier properties, thus representing a preferred embodiment of the invention.

[0015]

Unsaturated carboxylic acid derivatives often used as modifier include acrylic acid, methacrylic acid, maleic acid, fumaric acid, itaconic acid, crotonic acid, methyl maleic acid, methyl fumaric acid, mesaconic acid, citraconic acid, glutaconic acid, metal salts of the foregoing carboxylic acids, methyl hydrogen maleate, methyl hydrogen itaconate, methyl acrylate, ethyl acrylate, butyl acrylate, 2-ethylhexyl acrylate, hydroxyethyl acrylate, methyl methacrylate, 2-ethylhexyl methacrylate, hydroxyethyl methacrylate, aminoethyl methacrylate, dimethyl maleate, dimethyl itaconate, maleic anhydride, itaconic anhydride, citraconic anhydride, endo-bicyclo[2.2.1]-5-heptene-2,3-dicarboxylic acid, endo-bicyclo[2.2.1]-5-heptene-2,3-dicarboxylic anhydride, maleimide, N-ethylmaleimide, N-butylmaleimide, N-phenylmaleimide, glycidyl acrylate, glycidyl methacrylate, glycidyl ethacrylate, glycidyl itaconate, glycidyl citraconate, and 5-norbornene-2,3-dicarboxylic acid. Of these, preferred ones include unsaturated dicarboxylic acids and their anhydrides, of which maleic acid and maleic anhydride are particularly preferred.

[0016]

With no particular limitations on the method used to introduce these components containing functional groups into olefin compounds, an olefin compound to be used as major component may be copolymerized first with an olefin compound containing a functional group, or an unmodified polyolefin may be graft-copolymerized with an olefin compound containing a functional group using a radical initiator. Said component containing a functional group to be introduced should

preferably account for 0.001-40 mol%, more preferably 0.01-35 mol%, of the entire olefin monomers in the modified polyolefin.

[0017]

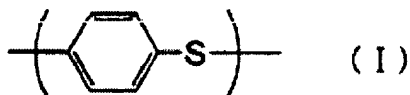
With no particular limitations on the method used to produce said (a) polyolefin resin, there are many useful processes including radical polymerization, coordination polymerization using a Ziegler-Natta catalyst, anionic polymerization, and coordination polymerization using a metallocene catalyst.

[0018]

Said (b) PPS resins to be used for the present invention are polymers that comprise repeating units as shown by the following structural formula (1):

[0019]

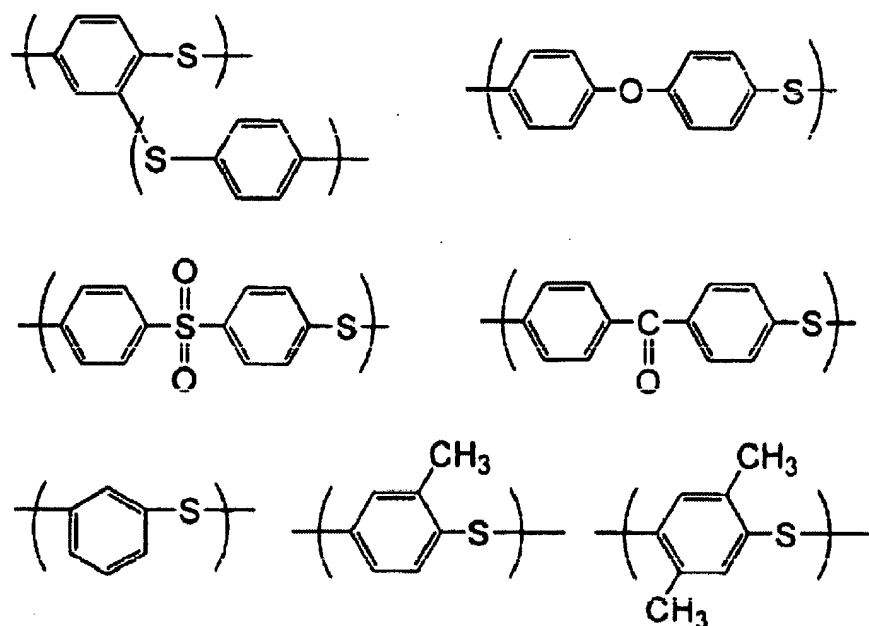
[Chemical formula 1]



To achieve a high heat resistance, said polymer component comprising a repeating unit as represented by the above structural formula should preferably account for 70 mol% or more, more preferably 90 mol% or more, of the entire polymer. In said PPS resins, a repeating unit as represented by the following structural formula may account for less than 30 mol% or so.

[0020]

[Chemical formula 2]



PPS polymers that partly consist of such a structure generally have a low melting point, so if thermoplastic resin with a low melting point is used as material for the non-barrier layer in the laminated structure according to the invention, said polymers are advantageous in terms of moldability.

[0021]

Though there are no specific limitations on the melt viscosity of PPS polymers used for the present invention as long as kneading of the melt can be performed, it is generally in the range of 50-20000 poise (320°C, shearing speed 1000 sec⁻¹), more preferably 100-5000 poise.

[0022]

Said PPS resins are generally produced by known methods including the process for production of polymers with a relatively small molecular weight described in Examined Patent Applications Publication (Kokoku) SHO 45-3368, and the processes for production of polymers with a relatively large molecular weight described in Examined Patent Applications Publication (Kokoku) SHO 52-12240 and

Patent Laid-Open Publication (Kokai) SHO 61-7332. For purposes of the invention, PPS resins as produced above may, before use, be subjected different treatment processes including crosslinking and chain extension by heating in air, heat treatment in an inert gas atmosphere such as nitrogen or under reduced pressure, washing with an organic solvent, hot water or an acid solution, activation with compounds containing a functional group such as acid anhydrides, amine, isocyanates, and disulfide compounds containing a functional group.

[0023]

Specifically, crosslinking or chain extension of PPS resin by heating can be performed in an atmosphere of a oxidizing gas such as air and oxygen, or in an atmosphere of a mixture of said oxidizing gas and an inert gas such as nitrogen and argon, in a heating container where the resin is heated at an appropriate temperature until a required melt viscosity is achieved. Heating is generally performed at a temperature of 170-280°C, more preferably 200-270°C, for a period of 0.5-100 hours, more preferably 2-50 hours, in most cases, but the two parameters may be controlled appropriately to achieve a required viscosity. Equipment used for said heating may be a hot air dryer or a rotation type or stirrer type heating system, of which rotation type or stirrer type heating equipment is preferred to ensure efficient, uniform processing.

[0024]

Specifically, heating of PPS resin in an inert gas atmosphere such as nitrogen or under reduced pressure may be performed by heating the resin in an inert gas atmosphere such as nitrogen or under reduced pressure at a heating temperature of 150-280°C, more preferably 200-270°C, for a heating time of 0.5-100 hours, more preferably 2-50 hours. Equipment used for said heating may be a hot air dryer

or a rotation type or stirrer type heating system, of which rotation type or stirrer type heating equipment is preferred to ensure efficient, uniform processing.

[0025]

PPS resin used for the present invention should preferably be deionized before use. Said deionization may be carried out by washing with an acid solution, washing with hot water, or washing with organic solvent, which may be performed in combination.

[0026]

The following methods can be used for washing PPS resin with an organic solvent. There are no specific limitations on the organic solvent to be used for washing of PPS resin unless it has unfavorable effects such as decomposition of the PPS resin, and preferred ones include: nitrogen-containing polar solvents including N-methylpyrrolidone, dimethylformamide, and dimethylacetamide; sulfoxide- or sulfone-based solvents including dimethylsulfoxide and dimethylsulfone; ketone-type solvents including acetone, methyl ethyl ketone, diethyl ketone, and acetophenone; ether type solvents including dimethyl ether, dipropyl ether, and tetrahydrofuran; halogen-based solvents including chloroform, methylene chloride, trichloroethylene, ethylene dichloride, and dichloroethane, tetrachloroethane, and chlorobenzene; alcohol and phenol type solvents including methanol, ethanol, propanol, butanol, pentanol, ethylene glycol, propylene glycol, phenol, cresol, and polyethylene glycol; and aromatic hydrocarbon type solvents including benzene, toluene, and xylene. Of the above organic solvents, preferred ones include N-methylpyrrolidone, acetone, dimethylformamide, and chloroform. These organic solvents are used solely or in combination. Washing with an organic solvent may be carried out by immersion of PPS resin in the organic solvent, while stirring or heating it

as required. There are no specific limitations on the washing temperature used to wash PPS resin with an organic solvent, and an appropriate temperature may be selected in the range from room temperature to about 300°C. The efficiency of washing generally increases with the washing temperature, but normally, required effect of washing is achieved at a washing temperature in the range from room temperature to 150°C. After the completion of washing with an organic solvent, the PPS resin should preferably be rinsed with warm water several times to remove the residual organic solvent.

[0027]

Hot water treatment of PPS resin can be carried out by the following methods. To achieve desired chemical modification of PPS resin by hot water washing, the water to be used should preferably be either distilled water or deionized water. Hot water treatment is normally performed by putting an appropriate amount of PPS resin in an appropriate amount of water, followed by heating and stirring under atmospheric pressure or in a pressure vessel. The amount of water should preferably be larger than that of PPS resin, and normally, one liter of water is used for every 200g or less of PPS resin.

[0028]

Acid treatment of PPS resin can be carried out by the following methods. Typically, such treatment may be carried out by immersion of PPS resin in an acid or an acid solution, while stirring or heating it as required. There are no specific limitations on the acid used unless it works to decompose the PPS resin, and preferred ones include: saturated aliphatic monocarboxylic acids including formic acid, acetic acid, propionic acid, and butyric acid; halogen-substituted saturated aliphatic carboxylic acids including chloroacetic acid and dichloroacetic acid; unsaturated aliphatic monocarboxylic acids including acrylic acid and crotonic acid; aromatic carboxylic acids

including benzoic acid and salicylic acid; dicarboxylic acids including oxalic acid, malonic acid, succinic acid, phthalic acid, and fumaric acid; and inorganic acid compounds including sulfuric acid, phosphoric acid, hydrochloric acid, carbonic acid, and silicic acid. Among others, acetic acid and hydrochloric acid are preferred. Acid treated PPS resin should preferably be washed several times with water or hot water to remove the residual acids and salts. Distilled water or demineralized water should preferably be used for the washing process to avoid impairment of desired modification brought by the acid treatment in the PPS resin.

[0029]

For purposes of the invention, a known conventional compatibilizer may be added with the aim of improving the compatibility between the polyolefin resin used as component (a) and the PPS resin used as component (b). Specifically, useful compatibilizers include: alkoxysilane and other organosilanes comprising at least one functional group selected from the group consisting of epoxy, amino, isocyanate, hydroxyl, mercapto, and ureido; random, block and graft copolymers and other modified polyolefins consisting of an α -olefin, such as ethylene and propylene, in combination with at least one compound selected from the group consisting of α,β -unsaturated carboxylic acids such as acrylic acid, methacrylic acid, maleic acid, and crotonic acid, and derivatives thereof such as esters, anhydrides, halides, sodium salts, potassium salts, magnesium salts, and zinc salts thereof; epoxy-containing olefin-based copolymers and multifunctional epoxy compounds, such as olefin-based copolymers consisting mainly of an α -olefin and a glycidyl ester of an α,β -unsaturated acid; which may be used in combination.

[0030]

There are no specific limitations on said (C) inorganic filler,

and fibrous, plate-like, powdery, and grainy fillers may be used. Specifically, useful fillers include: glass fiber; PAN- and pitch-based carbon fiber; metallic fibers such as stainless steel fiber, aluminum fiber and brass fiber; organic fibers such as aromatic polyamide fiber; fibrous or whisker-like fillers such as gypsum fiber, ceramic fiber, asbestos fiber, zirconia fiber, alumina fiber, silica fiber, titanium oxide fiber, silicon carbide fiber, rock wool, potassium titanate whisker, barium titanate whisker, aluminum borate whisker, and silicon nitride whisker; and powdery, grainy and plate-like fillers such as mica, talc, kaolin, silica, calcium carbonate, glass bead, glass flake, glass microballoon, clay, molybdenum disulfide, wollastonite, titanium oxide, zinc oxide, calcium polyphosphate and graphite. Of the above ones, glass fiber is used most widely, while PAN-based carbon fiber is preferred when electrical conductivity is required. There are no specific limitations on the type of glass fiber as long as it serves to reinforce common resins, and useful ones include, for instance, long- or short-fiber type chopped strands and milled fiber. Two or more selected from the above fillers may be used in combination. Said fillers for the invention may have their surface treated with a known coupling agent (such as silane- or titanate-based coupling agents) or other appropriate finishing agents.

[0031]

Glass fiber to be used may be sized or coated with thermoplastic resin such as ethylene/vinyl acetate copolymer, or thermosetting resin such as epoxy.

[0032]

The content of said fillers should preferably be in the range of 0-200 parts by weight, more preferably 5-200 parts by weight, and still more preferably 10-150 parts by weight, relative to the total

amount of polyolefin resin (a) and polyphenylene sulfide resin (b) which accounts for 100 parts.

[0033]

In the resin molding for gas and/or liquid barrier parts according to the invention, the polyolefin resin used as component (a) and the PPS resin used as component (b) should account for 5-80 vol% and 95-20 vol%, respectively, in order to produce a desired phase structure (for instance, a sea-island structure) wherein the PPS resin component forms a continuous phase (matrix phase) while the polyolefin resin component forms a distribution phase. Here, if the PPS resin accounts for a smaller portion, such as in a structure consisting of 55-80 vol% polyolefin resin and 45-20 vol% PPS resin, a phase structure comprising a continuous phase of the PPS resin can be produced by appropriately controlling the melt viscosity ratio between the polyolefin resin and the PPS resin. A molding comprising such a phase structure is particularly preferred because it can achieve a good balance among properties after absorbing water, and barrier properties. Further, said polyolefin resin and said PPS resin should more preferably account for 60-75 vol% and 40-25 vol%, respectively, while maintaining a phase structure as described above. If said polyolefin resin used as component (a) accounts for more than 80 vol%, the PPS resin component cannot form a continuous phase that characterizes the resin moldings according to the invention, making it impossible to achieve the goal of the invention. If said polyolefin resin used as component (a) accounts for less than 5 vol%, on the other hand, the toughness of the resin moldings will decrease, resulting in undesirable results.

[0034]

To produce a phase structure (for instance, a sea-sea structure) consisting of a PPS resin component and a polyolefin resin component,

each forming a virtually continuous phase (matrix phase), it is important to control the melt viscosity and compatibility of the polyolefin resin and the PPS resin while maintaining the percentage proportion in the range of 15-85 vol% polyolefin resin and 85-15 vol% PPS resin. To produce a phase structure as described above, the composition should preferably be in the range of 30-70 vol% polyolefin resin and 70-30 vol% PPS resin, more preferably 35-65 vol% polyolefin resin and 65-30 vol% PPS resin. If said polyolefin resin used as component (a) accounts for more than 85 vol%, it will be difficult for the PPS resin component to form a virtually continuous phase, making it impossible to achieve the goal of the invention. If said polyolefin resin used as component (a) accounts for less than 15 vol%, on the other hand, it will be difficult for the polyolefin resin component to form a virtually continuous phase.

[0035]

To allow the polyolefin resin component to form a continuous phase (matrix phase) while allowing the PPS resin component to form a zonal distribution phase (laminar structure), the composition should preferably be in the range of 55-95 vol% polyolefin resin and 45-5 vol% PPS resin, more preferably 60-90 vol% polyolefin resin and 40-10 vol% PPS resin, and still more preferably 65-85 vol% polyolefin resin and 35-15 vol% PPS resin. If the polyolefin resin used as component (a) accounts for more than 95 vol%, it will be difficult for the PPS resin component to form a zonal distribution phase with a sufficient length and size, making it impossible to achieve the goal of the invention. If the polyolefin resin used as component (a) accounts for less than 55 vol%, on the other hand, it will be difficult for the polyolefin resin to form a zonal distribution phase.

[0036]

A conductive filler or a conductive polymer may be added to impart electrical conductivity to the resin molding for gas and/or liquid barrier parts according to the invention, and there are no specific limitations on the conductive filler as long as it serves to impart electrical conductivity to common resins, such fillers including metal powder, metal flake, metal ribbon, metal fiber and metal oxide, in addition to inorganic filler, carbon powder, graphite, carbon fiber, carbon flake and scaly carbon that are coated with conductive material.

[0037]

Said metal powder, metal flake and metal ribbon may be made of metal species such as silver, nickel, copper, zinc, aluminum, stainless steel, iron, brass, chrome, and tin.

[0038]

Said metal fiber may be made of metal species such as iron, copper, stainless steel, aluminum, and brass.

[0039]

Said metal powder, metal flake, metal ribbon and metal fiber may be surface-finished with a titanate-, aluminum- or silane-based finishing agent.

[0040]

Useful metal oxides include SnO_2 (antimony doped), In_2O_3 (antimony doped) and ZnO (aluminum doped), which may be surface-finished with a titanate-, aluminum- or silane-based finishing agent.

[0041]

Useful conductive materials to coat inorganic fillers include aluminum, nickel, silver, carbon, SnO_2 (antimony doped) and In_2O_3 (antimony doped). Useful inorganic fillers to be coated include mica, glass bead, glass fiber, carbon fiber, potassium titanate whisker, barium sulfate, zinc oxide, titanium oxide, aluminum borate

whisker, zinc oxide whisker, titanium oxide whisker, and silicon carbide whisker. Useful coating methods include vacuum evaporation, sputtering, electroless deposition, and baking. These may be finished with a titanate-, aluminum- or silane-based finishing agent.

[0042]

Carbon power may be in the form of acetylene black, gas black, oil black, naphthalene black, thermal black, furnace black, lamp black, channel black, roll black, or disk black, which may be produced by different methods from different materials. There are no specific limitations on the material or method to be used to produce said carbon powder, but acetylene black and furnace black are particularly preferred. A variety of carbon powder products with different properties in terms of particle size, surface area, DBP absorption, and ash content are available. There are no specific limitations on the properties of the carbon powder to be used for the invention, but products with an average particle diameter of 500 nm or less, preferably in the range of 5-100 nm, more preferably 10-70 nm, are generally used to achieve a good balance between the strength and the electrical conductivity. Their surface area (BET method) should preferably be 10 m²/g or more, more preferably 30 m²/g or more. The amount of DBP addition should preferably be 50 ml/100g or more, more preferably 100 ml/100g or more. The ash content should preferably be 0.5% or less, more preferably 0.3% or less.

[0043]

These carbon powder products may be finished with a titanate-, aluminum- or silane-based finishing agent. They may be palletized to facilitate their handling in performing melt kneading.

[0044]

Moldings produced by processing the resin composition for gas and/or

liquid barrier parts according to the invention are frequently required to have surface smoothness. To achieve this, conductive fillers to be used for the invention should, as in the case of inorganic filler (C) for the invention, preferably be in the form of powder, particle, plate, scale, or fiber having a length to diameter ratio of 200 or less in the resin composition, rather than ordinary fibrous fillers which are high in aspect ratio.

[0045]

Useful conductive polymers for the invention include polyaniline, polypyrrole, polyacetylene, polyparaphenylene, polythiophene and polyphenylene vinylene.

[0046]

The above conductive fillers and/or conductive polymers may be used in combination. Of the above conductive fillers and conductive polymers, carbon black is particularly preferred in terms of strength and cost.

[0047]

The optimum content of these conductive fillers and/or conductive polymers used for the invention depends on the type of the conductive fillers and/or conductive polymers used and cannot be identified specifically, but they should preferably be in the range of 1-250 parts by weight, more preferably 3-100 parts by weight, relative to the total of components (A), (B) and (C) which accounts for 100 parts by weight, to achieve a good balance among electrical conductivity, flowability and mechanical strength.

[0048]

Fillers coated with conductive material should preferably have a volume resistivity of $10^{10} \Omega \cdot \text{cm}$ or less to maintain a required antistatic capability. The addition of such a conductive filler or conductive polymer, however, can cause a decrease in strength

and flowability in most cases. So, the content of said conductive filler or conductive polymer should be as small as possible if the required conductivity level is achieved. The required conductivity is normally more than $100 \Omega \cdot \text{cm}$ and not more than $10^{10} \Omega \cdot \text{cm}$, depending on the uses of the product.

[0049]

If having no adverse influence on the effect of the invention, the composition according to the invention may contain other components including antioxidant, thermal stabilizer (based on hindered phenol, hydroquinone, phosphite, substitution products thereof, etc.), weathering agents (based on resorcinol, salicylate, benzotriazole, benzophenone, hindered amine, etc.), mold release agents/lubricants (montanoic acid, metal salts thereof, esters thereof, half esters thereof, stearyl alcohol, stearamide, various bisamides, bis-urea, polyethylenewax, etc.), pigments (cadmium sulfide, phthalocyanine, carbon black, etc.), dyes (nigrosin, etc.), crystal nucleation agents (talc, silica, kaolin, clay, etc.), plasticizers (p-octyl hydroxybenzoate, N-butylbenzene sulfonamide, etc.), antistatic agents (alkyl sulfate type anionic antistatic agents, quaternary ammonium salt type cationic antistatic agents, nonionic antistatic agents such as polyoxyethylene sorbitan monostearate, betaine-based ampholytic antistatic agents, etc.), flame retardants (for instance, red phosphorus, melamine cyanurate, magnesium hydroxide, aluminium hydroxide, other hydroxides, ammonium polyphosphate, brominated polystyrene, brominated polyphenylene ether, brominated polycarbonate, brominated epoxy resin, and mixtures of these bromine-based flame retardants and antimony trioxide), and other polymers.

[0050]

There are no specific limitations as long as it is possible to produce

a resin molding that meet the requirements specified for the invention, but a desired dispersion state during the melt kneading process can be achieved, for instance, by using a biaxial extruder for melt kneading wherein polyolefin resin and PPS resin are supplied through the main feeder while an inorganic filler is supplied through a side feeder provided at the end of the extruder, or by first carrying out melt kneading of polyolefin resin and PPS resin, followed by melt kneading along with an inorganic filler.

[0051]

There are no specific limitations on the molding method to be used for the resin molding for gas and/or liquid barrier parts according to the invention, and known methods such as injection molding, extrusion, blow molding and press molding may be used, but injection molding, injection compression molding, and compression molding are preferred for efficient manufacturing. The molding temperature to be adopted is normally 5-50°C above the melting point of the PPS resin used, and the intended molding comprises one layer in most cases while multiple layered moldings may be produced by using a two-color molding process.

[0052]

There are no specific limitations on the arrangement of the different layers in the resin molding according to the invention, and all layers may comprise the resin molding for gas and/or liquid barrier parts according to the invention while additional layers may comprise other thermoplastic resin or a filler-free resin molding for gas and/or liquid barrier parts. In the case of a two-layer molding, the layer comprising the resin molding for gas and/or liquid barrier parts should preferably be the innermost layer to maximize the effect of its barrier properties.

[0053]

Thermoplastic resin materials that can be used for layers other than those of the resin molding for gas and/or liquid barrier parts according to the invention include saturated polyester, polysulfone, polytetrafluoroethylene, polyetherimide, polyamide imide, polyamide, polyketone copolymer, polyphenylene ether, polyimide, polyethersulfone, polyether ketone, polythioether ketone, polyether ether ketone, thermoplastic polyurethane, polyolefin, ABS, polyamide elastomer, and polyester elastomer, which may be used solely, in combination, or with other additives to develop desired properties. Resulting moldings may be adhered or welded with each other or with other moldings, and conventional methods can be used for these processes, with no specific limitations.

[0054]

The resin molding for gas and/or liquid barrier parts according to the invention, even in a water-containing state, is favorably low in permeability to gas, liquid and/or vaporized material such as fluorocarbon 11, fluorocarbon 12, fluorocarbon 21, fluorocarbon 22, fluorocarbon 113, fluorocarbon 114, fluorocarbon 115, fluorocarbon 134a, fluorocarbon 32, fluorocarbon 123, fluorocarbon 124, fluorocarbon 125, fluorocarbon 143a, fluorocarbon 141b, fluorocarbon 142b, fluorocarbon 225, fluorocarbon C318, R-502, 1,1,1-trichloroethane, methyl chloride, methylene chloride, ethyl chloride, methylchloroform, propane, isobutane, n-butane, dimethyl ether, castor oil based brake fluid, glycol ether based brake fluid, borate based brake fluid, brake fluid for arctic use, silicone oil based brake fluid, mineral oil based brake fluid, power steering oil, window washer liquid, gasoline, methanol, ethanol, isobutanol, butanol, nitrogen, oxygen, hydrogen, carbon dioxide, methane, propane, natural gas, argon, helium, xenon, and pharmaceuticals, and accordingly serves as material for fuel tank, oil reservoir

tank, other chemicals storage containers and attachment thereto (for instance, bottle and attached pump thereto for different liquids such as shampoo, rinse, and liquid soap), different fuel tube connectors, engine oil tube connectors, brake hose connectors, window washer liquid nozzle, coolant/refrigerant pipe connectors for refrigerators, pipe connectors for air-conditioner refrigerant, connectors for tubes for extinguishers and fire-fighting equipment, connectors and valves for tubes for medical refrigerators, other tubes for liquid and gas transportation, other gas-barrier products including containers for storing medical and chemical liquids, automobile parts, engine parts, housing of electric tools, other mechanical parts, electric and electronic parts, medical supplies, food containers, household goods, office supplies, building material, furniture parts, and many other products.

[0055]

[Examples]

Hereinafter, the present invention is described more in detail by reference to examples, which however are not intended to limit the present invention.

(1) Barrier properties against alcohol gasoline blend

A 40 mm diameter extruder consisting of a die for tube molding installed at the end of the extruder, a sizing die to cool the tube and control its size, and take-up equipment was used to mold a tube with an outside diameter of 8 mm and an inside diameter of 6 mm. A piece with a length of 20 cm was cut out of the tube, and after closing one end, filled with a precisely weighed 6g amount of an alcohol gasoline blend consisting of 75:25 (weight ratio) of commercial regular-class gasoline and ethanol, followed by closing the other end. Subsequently, the test piece was weighed, and placed in an explosion proof type oven adjusted to 60°C, and after 500

hours, the decrease in weight was measured.

(2) Barrier properties against oxygen

An analyzer (GTR-10, supplied by Yanaco Analytical Instruments Corporation) was used according to the differential pressure method specified in JIS K7126A.

(3) Material strength

Measurement was conducted according to the following standard method.

Tensile strength: ASTM D638

Flexural modulus: ASTM D790

Izod impact strength: ASTM D256

(4) Observation of phase structure

A cross-section of the tube molding was observed by transmission electron microscopy (TEM).

[0056]

The polyolefin resins and PPS resins used in examples and comparative examples are as follows.

<Polyolefin resin>

(PO-1): High density polyethylene with a melt index (MI) of 14 and a density of 0.96.

(PO-2): High density polyethylene with a MI of 32 and a density of 0.96.

(PO-3): Polypropylene with a MI of 10 and a density of 0.89.

<PPS resin>

(PPS-1): PPS resin with a melting point of 280°C and a weight average molecular weight (Mw) of 30000.

(PPS-2): PPS resin with a melting point of 280°C and a Mw of 49000.

(PPS-3): PPS resin with a melting point of 280°C and a Mw of 70000.

Examples 1-12 and comparison examples 1-4

As shown in Tables 1 and 2, PPS resin and a compatibilizer (90/10

(wt%) ethylene/glycidylmethacrylate copolymer) were mixed, supplied along with polyolefin resin through the main feeder of a Japan Steel Works TEX30 biaxial extruder, while an inorganic filler, if used, is supplied through a side feeder at a mid portion of the cylinder, followed by melt kneading at a kneading temperature of 300°C and a screw revolution speed of 200 rpm. The pellets obtained were dried, and supplied to injection molding equipment (IS100FA, supplied by Toshiba Machine, mold temperature 80°C) to produce test specimens. Measured barrier properties and material strength of the specimens are shown in Tables 1 and 2.

[0057]

In the table, GF and MF represent glass fiber (fiber diameter 10 μm , 3 mm chopped strands, supplied by Nippon Denki Glass Co.) and milled fiber (average fiber length 140 μm , average fiber diameter 9 μm , supplied by Nippon Denki Glass Co.), respectively.

[0058]

[Table 1]

Components	Item	Unit	Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Comparison example 1	Comparison example 2
	Type of polyolefin resin Content	— vol%	PO-1 67	PO-2 56	PO-1 78	PO-3 62	PO-1 67	PO-1 34	PO-1 100	PO-2 67
	Type of PPS resin Content	— vol%	PPS-2 30	PPS-1 40	PPS-1 20	PPS-1 35	PPS-1 30	PPS-2 60	—	PPS-3 30
	Compatibilizer	vol%	3	4	2	3	3	6	—	3
Material strength	Phase structure		PPS matrix	PPS and polyolefin matrix	PPS zonal distribution	PPS matrix	PPS and polyolefin matrix	PPS and polyolefin matrix	Polyolefin matrix	Polyolefin matrix
	Alcohol gasoline blend permeability	G	0.5	0.7	0.8	0.6	0.6	0.4	3.3	2.8
	Oxygen permeability	Note 1	40	60	80	40	50	15	10000	9000
	Tensile strength	MPa	45	55	40	60	45	70	30	35
	Flexural modulus	Gpa	2.2	2.5	2.0	2.6	2.0	2.7	1.0	1.5
	Izod impact strength	J/m	50	56	44	42	45	40	30	28

Note 1: Oxygen permeability is represented in cc·25μ/m² 24 hrs·atm, 25°C.

(PO-1): High density polyethylene with a MI of 14 and a density of 0.96.

(PO-2): High density polyethylene with a MI of 32 and a density of 0.96.

(PO-3): Polypropylene with a MI of 10 and a density of 0.89.

(PPS-1): PPS resin with a melting point of 280°C and a Mw of 30000.

(PPS-2): PPS resin with a melting point of 280°C and a Mw of 49000.

(PPS-3): PPS resin with a melting point of 280°C and a Mw of 70000.

[0059]

[Table 2]

Components	Item	Unit	Example 7	Example 8	Example 9	Example 10	Example 11	Example 12	Comparison example 3	Comparison example 4
	Type of polyolefin resin Content	— vol%	PO-1 67	PO-2 56	PO-1 78	PO-3 62	PO-1 67	PO-1 34	PO-1 100	PO-2 67
	Type of PPS resin Content	— vol%	PPS-2 30	PPS-1 40	PPS-1 20	PPS-1 35	PPS-1 30	PPS-2 60	—	PPS-3 30
	Compatibilizer	vol%	3	4	2	3	3	6	—	3
	Type of inorganic filler Content	— wt%	GF 40	GF 40	GF 40	GF//talc 35//5	GF//MF 30//10	GF 40	GF 40	GF 40
Material strength	Phase structure		PPS matrix	PPS and polyolefin matrix	PPS zonal distribution	PPS matrix	PPS and polyolefin matrix	PPS and polyolefin matrix	Polyolefin matrix	Polyolefin matrix
	Alcohol gasoline blend permeability	g	0.4	0.6	0.7	0.5	0.6	0.3	3.2	2.5
	Oxygen permeability	*1	40	60	70	40	50	10	10000	9000
	Tensile strength	MPa	110	110	100	95	90	115	100	110
	Flexural modulus	GPa	6.3	7.0	6.1	5.5	5.2	7.8	5.4	6.0
	Izod impact strength	J/m	90	100	95	90	85	100	90	80

Note 1: Oxygen permeability is represented in cc·25μ/m² 24 hrs·atm, 25°C.

(PO-1): High density polyethylene with a MI of 14 and a density of 0.96.

(PO-2): High density polyethylene with a MI of 32 and a density of 0.96.

(PO-3): Polypropylene with a MI of 10 and a density of 0.89.

(PPS-1): PPS resin with a melting point of 280°C and a Mw of 30000.

(PPS-2): PPS resin with a melting point of 280°C and a Mw of 49000.

(PPS-3): PPS resin with a melting point of 280°C and a Mw of 70000.

Results of examples 1-12 and comparative examples 1-4 show that the resin molding comprising a specific phase structure as specified for the present invention has excellent barrier properties that ensure high practicability.

[0060]

[Effect of the invention]

The resin molding according to the present invention has good gas and/or liquid barrier properties and serves as material for different uses including electric and electronic equipment, precision machinery, office equipment, automobile and vehicle parts, buildings, packaging, furniture, and sundries.



[Title of the document] Abstract

[Abstract]

[Problem]

To provide a resin molding for gas and/or liquid barrier parts that has specifically-enhanced barrier properties against liquid chemicals and gas, while maintaining intrinsic features of polyolefin resin such as high toughness and moldability.

[Means of solving the problem]

A resin molding for gas and/or liquid barrier parts comprising a resin composition that consists of 100 parts by weight of a resin composition component consisting of (a) 5-80 vol% of polyolefin resin and (b) 95-20 vol% of polyphenylene sulfide resin, in combination with (c) 0-200 parts by weight of an inorganic filler, wherein the phase structure as observed by electron microscopy comprises (b) a matrix phase (continuous phase) of said polyphenylene sulfide resin and (a) a distribution phase of said polyolefin resin.

[Selected drawings]

None